THE SODIUM EXPOSURE TEST CELL TO DETERMINE OPERATING PARAMETERS FOR AMTEC ELECTROCHEMICAL CELLS

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ABSTRACT

The Sodium Exposure Test Cell (SETC) is a non-power producing cell which has been developed to evaluate and test components of the electrochemical cell in an Alkali Metal Thermal to Electric Converter. Performance and time dependence of performance of the electrode and the electrolyte in AMTEC cells can be tested in an SETC, and performance parameters which correlate with those taken from AMTEC operation can be calculated from data taken in an SETC.

INTRODUCTION

AMTEC, the Alkali Metal Thermal to Electric Converter, is a direct energy conversion device capable of near-Carnot efficiencies; it has been demonstrated to perform at high power densities, with open circuit voltages in single electrochemical cells up to 1.6 V and current densities up to 2.0 A/cm^2 [Weber, 1974; Cole, 1983]. As a power system, AMTEC is expected to deliver 20-25 W/kg. The work described in this paper is part of a study to determine the suitability of AMTEC power conversion in NASA's X2000 spacecraft program for exploration of the Solar System's outer planets.

The lifetime of the electrochemical cell in an AMTEC system depends on the rate of degradation of individual components as well as the interactions of components. The electrode, current collection network and beta"-alumina solid electrolyte (BASE) all degrade somewhat over time at typical AMTEC operating temperatures (900 - 1200 K); in addition, the components interact with each other and operation of the components in sodium vapor atmosphere influences the performance of the electrochemical cell as well as the rate of its performance degradation. We have studied the components individually as well as in AMTEC cells and at AMTEC operating conditions in order to understand the interactions among the components and the degradation mechanisms in the electrochemical cell. There are substantial materials issues which must be taken into consideration in selecting components of the electrochemical cell, as release of volatile materials from one component can play a significant role in degradation of other components in the cell.

The components of the AMTEC electrochemical cell to be considered here include the electrode, with emphasis on the cathode, β"-alumina solid electrolyte (BASE), the current collection network, and the containment. Other components which must be considered but will not be treated here include the condenser, the wick/pumping system, the braze joints and the feedthroughs.

Determining the operating performance of individual components in an AMTEC cell is a challenging task, as there are many components and the likelihood of interaction among them is great. To isolate components and determine degrees of interaction, we have developed the Sodium Exposure Test Cell (SETC). The SETC has been used for several experiments, particularly to develop an electrode life model
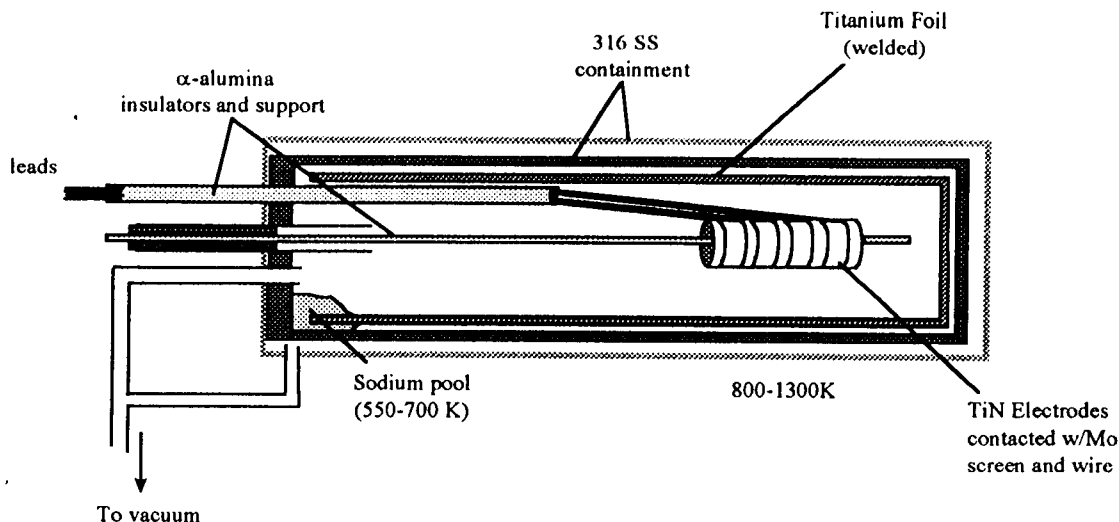
Figure 1: The Sodium Exposure Test Cell

and to test new electrode materials [Ryan, 1992]. The SETC also plays an important role in accelerated testing to develop life models for other components, to determine the modes of interaction among components, and finally to verify life models.

The Sodium Exposure Test Cell

A diagram of an SETC is shown in Figure 1. The containment consists of a stainless steel tube lined with titanium foil. The titanium foil is welded closed the entire length of the stainless steel tube and at the closed end of the tube. The purpose of the Ti foil is to prevent entry of elements volatilized from the steel. Previous work has shown that trace elements in steel, particularly Mn and Cr, will volatilize at relatively low temperatures, 650 - 800 K, and react with electrode materials [Ryan, 1993] and with BASE.

The electrochemical cell in an SETC is not a power producing cell. It consists of a series of electrodes on a section of BASE. A typical experiment includes two sections of BASE, each with four electrodes about 0.5 cm wide and separated by abut 0.25 cm. Generally, the two sections of BASE have different electrode materials, and the experiment allows direct comparison of their performance. The

BASE section is supported in the Ti/steel container on an α-alumina rod. The electrodes are individually contacted by wrapping Mo screen around them and tying them with Mo wire. Mo wire leads are brought out of the cell through α-alumina insulators.

The cell is operated in low pressure Na vapor by creating a potential difference between electrodes and measuring the current of sodium oxidation at the anode and of sodium ion reduction at the cathode. Sodium ions are conducted axially along the BASE tube. The electrochemical cell is shown schematically in Figure 2.
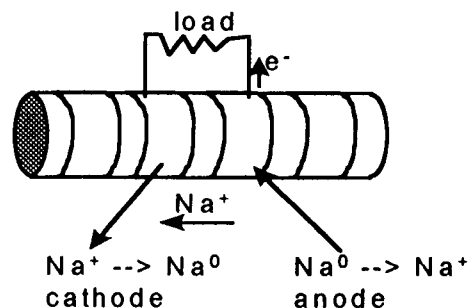
Figure 2: The electrochemical cell in an SETC.

The α-alumina insulators are held in a stainless steel manifold consisting of several steel tubes through which alumina insulators can pass. The insulating alumina tubes are held in the manifold with Epoxy-Patch insulating epoxy, which forms

a vacuum tight seal and will endure temperatures up to 200°C. The steel manifold is welded to the steel tube .containing the Ti liner and the electrochemical cell. This assembly is then placed in a second steel tube, and then second tube is welded to the manifold. The manifold includes a pump out port and a sodium fill port. The outer steel tube includes a pump out port. Several thermocouples are attached to the BASE tubes and at the manifold.

The SETC is evacuated to 1×10^{-4} Pa then baked .at ~ 400°C to ensure that water is removed. After baking, ~ 10 g of liquid sodium at ~125°C is pushed into the cell using argon. The sodium stays in a pool at the manifold, where control of the temperature using heating tapes will control the sodium vapor pressure in the cell. Thermocouples are placed so that they will be in contact with the liquid sodium pool.

Measurements in the SETC

There are two types of measurements made on the electrochemical cell in an SETC, controlled potential current-voltage curves (iV curves) and Electrochemical Impedance Spectroscopy (EIS).

IV Curves

iV curves may be measured in a two-electrode or a four-electrode configuration, although the two electrode configuration is more common. In this measurement, a potential difference is applied between two electrodes, and the current of sodium oxidation and reduction measured at the working electrode. The potential is swept from 0.0 V, so that the working electrode is negative with respect to the counter electrode, to produce cathodic current at the working electrode until limiting current is reached. The sweep is reversed to force anodic current at the working electrode until a limiting current is reached, and the potential returned to 0.0 V.
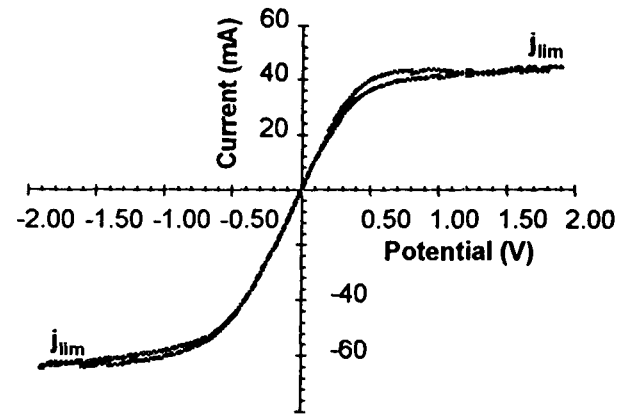
Figure 3: An iV curve on sputtered TiN electrodes

The primary information taken from a two-electrode iV curve is the morphology factor, G [Williams, 1990b]. In many electrode materials used in an AMTEC cell, G is not, strictly speaking, a geometric factor which measures pore size, but rather is a measure of impedance to sodium transport from the electrode-electrolyte interface to the vapor space. G can be calculated from the limiting current j_{lim} in the two-electrode iV curve. A typical iV curve is shown in Figure 3, and the method of calculation of G shown in Equation 1. Equation 1 is derived from equations 6 and 7 in Ref (Williams, 1990b).

$$G = \left[\frac{P_{Na} (T_{el}/T_{Na})^{1/2} F}{j_{lim} (2\Pi MRT_{el})^{1/2}} - 1 \right] \frac{8\Pi}{3} \quad (1)$$

where P_{Na} is the vapor pressure of sodium in the SETC, calculated from the saturated vapor pressure of the sodium pool temperature, T_{Na}, T_{el} is the temperature of the electrode, F is the Faraday, M the molecular weight of Na, and R the gas constant.

Four-electrode iV curves may also be measured, where voltage is measured between the inner electrodes while current flows between the outer electrodes. The slope of the curve through 0.0 V may be used to determine the resistance in the electrode. The four electrode configuration eliminates the series resistance

from the measurement, and so the series resistance in the cell may be calculated by comparing two and four probe iV curve slopes. The series resistance consists of the contact resistance between the Mo screen and the electrode, the contact resistance between the Mo screen and the lead, the resistance of the lead, and the contact resistance between the lead and the lead to the potentiostat.

Electrochemical Impedance Spectroscopy

EIS is used in both two and four lead configurations. In the two lead configuration, the impedance at 0.0 VDC is measured using a 5 - 10 mVAC perturbation, over a range from 0.1 Hz to 64 kHz. A typical Nyquist plot ($-Z_{imaginary}$ vs. Z_{real}), shown in Figure 4 can be used to determine the series resistance, R_S, and the apparent charge transfer resistance, R_{ACT}, at open circuit. R_S is the value of the high frequency intercept on the real axis (Z_{re}), and R_{ACT} is the difference of the value of Z_{re} at low frequency and at high frequency. The exchange current density at open circuit (overpotential, η = 0, no net current owing to sodium reduction) J_0, can be calculated from R_{ACT}, using equation 2.
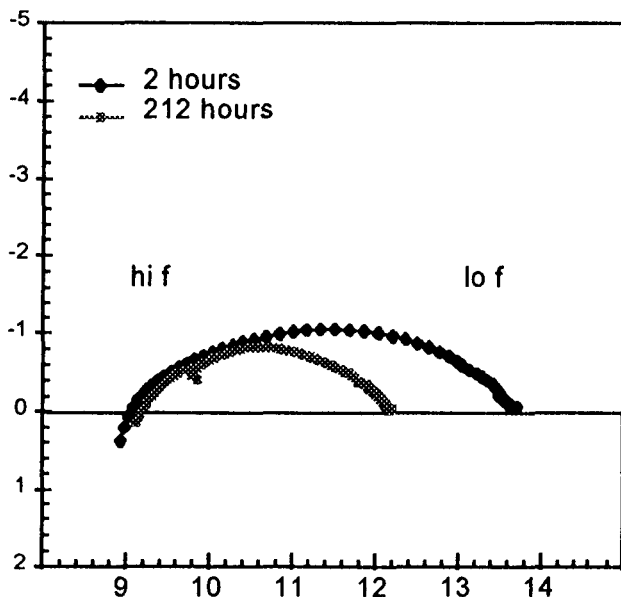

Figure 4: Nyquist plot of sputtered TiN at 0.0VDC. T_{el}= 1123 K; T_{Na} = 575 K.

$$J_0 = RT_{el}/FR_{ACT} \qquad (2)$$

J_0^0, is the exchange current density at an equilibrium potential obtained with satureated sodium vapor in contact with the electrode.

$$J_0^0 = J_0 (P_{el}/P_{Na})^{1/2} \qquad (3)$$

B, the exchange current density normalized to the sodium collision rate and reaction rate at unit activity sodium, can be calculated from equation 2 and 3 to yield equation 4 [Williams, 1990a].

$$B = J_0^0/ P_{el} T_{el}^{1/2} \qquad (4a)$$

or, directly from R_{ACT},

$$B = \left[\frac{(T_{el})}{P_{el}P_{Na}} \right]^{1/2} \left[\frac{RT_{el}}{R_{ACT} F} \right] \qquad (4b)$$

B has been observed to be approximately constant, 90 - 150 $AK^{1/2}/m^2Pa$ for several electrode materials, and can be correlated to electrode performance [Williams, 1990a]. Over the temperature range 900-1200 K, B is approximately independent of electrode temperature, and can be used as a measure of the performance of an electrode. It is a sensitive measure of the interfacial impedance, and thus large changes in B will be reflected as relatively small changes in electrochemical cell performance until exchange current drops significantly. An empirical relationship of electrode power to B has shown that B can drop from an initial value of 100 to 30 $AK^{1/2}/m^2Pa$ with only 15-20% drop in electrode specific power [Ryan, 1993]. This relationship was developed from both AMTEC cells and SETC experiments.

BASE Ionic Conductivity

In the four lead configuration, EIS is used to determine the ionic conductivity, σ, of the BASE. As the high frequency intercept of the impedance plot corresponds to the resistance

in the BASE, at 0.0 V it represents the ionic resistance between the leading edges of the two center electrodes. The ionic conductivity is the reciprocal of the resistivity, where the distance between the leading edges of the electrodes are the distance the ions travel.

RESULTS AND DISCUSSION

Recent studies using the SETC have included operation of two formulations of TiN at 1123 K for 1000 hours and at 1223 K for 500 hours. 2 probe iV curves and 2 and 4 probe EIS were taken and electrode and electrolyte parameters calculated for each formulation, and are reported in Table 1. G and B for the two formulations of TiN electrodes were calculated at 1123 K. The Na pressure in the higher temperature experiment was not well known, and so it was not possible to calculate a reliable value for G or B in that experiment.

Electrolyte ionic conductivity, σ, was calculated from 4 probe EIS data, and is also reported in Table 1. The plot in Figure 5 shows BASE σ in three different experiments. The 1223 K experiment shows a marked drop in σ in the first hundred hours of high temperature operation. While we consider this drop to be real, it may have been a result of soda loss caused by low sodium pressure in the cell, and so must be repeated to confirm whether σ drops rapidly at 1223 K.

With performance parameters derived from the measurements taken in an SETC experiment, life limiting processes in AMTEC cell components can be isolated and elucidated. Earlier experiments which showed rapid drop off in electrode performance, as evidenced by rapid drop in B, were analyzed by physical methods such as Scanning Electron Microscopy (SEM), elemental analysis and X-Ray Diffraction (XRD) of electrodes after the experiment. The rapid drop was found to have been caused by reaction of the electrode material with volatile materials in the containment, specifically Mn and Cr [Ryan, 1992]. This information was used to recommend refractory metal containment for AMTEC cells.

The recent SETC experiments on TiN electrodes have also shown a decrease in the series resistance in the course of an experiment. This decrease is attributed to interdiffusion of the current collection network and the electrode and the corresponding drop in the contact resistance, confirmed by SEM after the experiment.

SETC experiments continue to determine whether there is significant interaction of the electrode or BASE with components of the braze materials.

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TABLE I: Electrode and Electrolyte Performance Parameters from SETC Experiments

	TiN 9/93 sputtered 1123 K	TiN 9/97 sputtered 1123 K	TiN 9/97 Weber 1123K	TiN 3/98 sputtered 1223 K	RhW 1/94 sputtered 1123K
B 25 hours	60	75	70		180
B 500 hours	60	50	40		110
B 1000 hours	50	50	50		100
$(AK^{1/2}m^{-2}Pa^{-1})$					
G 25 hrs	50	70	10-20	10	
G 500 hrs	50	50	10-20	10	
G 1000 hrs	50	50	10-20	10	
σ (S/cm) 25 hrs		.55		.54	.54
σ 500 hrs		.54		.38	.54
σ 1000 hrs		.50			.56